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# Dynamic Study of N'N-dimethylparanitroaniline encapsulated in Silicalite-1 matrix using neutron spin-echo spectroscopy

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**Abstract.** The present work focuses on the dynamic studies of N'N-dimethylparanitroaniline (dmpNA) encapsulated in silicalite zeolite. Quasielastic neutron scattering (QENS) experiments are carried out using neutron spin-echo technique. Polarisation of the scattered neutron beam is measured at carefully chosen values of Q=0.35, 0.9, 1.1 and 1.45 Å$^{-1}$ at fixed T=298 K and at fixed Q=0.9 Å$^{-1}$ at 150, 200, 250 and 298 K. This gives insight into the motion and the related activation energy of the guest dmpNA molecule. The quasielastic signal observed in the present system within the time range considered is due to fast local rotational motions of protons of the end methyl groups. The results are in good agreement with the dynamics of methyl group rotations reported in the literature by backscattering QENS technique.

## 1 Introduction

Zeolites can be ideal hosts for a large variety of photochemically and photophysically active organic dye molecules as guests[1]. An important advantage of dye-zeolite composites is the protection of the dye molecules against chemical attack, photobleaching, thermal decomposition or photo isomerisation[2]. Among the numerous potential applications of these hybrid materials, dye-loaded zeolite may find a new use as stabilized, environment-friendly pigments. In this perspective one of such pigments, as an analogue of Maya-blue, was recently synthesized in our laboratory and showed high stability towards chemical and thermal attack[3].

The color can be durably fixed by trapping or encapsulating the organic dye in a zeolite matrix; the hybrid materials combine then the properties of the microporous mineral substrate (host) and the colour of the organic dye (guest)[4]. One industrial application could be the replacement of actual inorganic pigments containing hazardous, water-soluble transition metals such as cadmium and mercury[5] by new inert hybrid materials. In such systems, one would tune the colour and stability by a careful choice of the porosity of the host and native optical properties of the guest[6]. Hence, a detailed knowledge of the structure and intermolecular interaction is a prerequisite for understanding the performance of these materials.

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We choose as a case study the model system (dmpNA@MFI) where the guest hyperpolarisable dmpNA molecule is encapsulated in pores of silicalite zeolite (MFI topology). The precise location of dmpNA molecules within the zeolite channels using powder X-ray diffraction methods is under study. In the current paper, we concentrate on the dynamic properties of the dmpNA@silicalite hybrid in terms of the local and translational movements of the guest molecule. The quasielastic neutron scattering (QENS) has already been applied extensively for studying the movements of organic molecules inside zeolite channels[7]. In the present work, we study by neutron spin echo (NSE) spectroscopy the dynamics of N'N-dimethyl-paranitroaniline (dmpNA) inside the channel network of a siliceous MFI. We focus on a fast motion (time scale of picoseconds), of the order of the methyl group re-orientation within the dmpNA molecule, relying on the incoherently scattered signal from the H atoms.

## 2 Experimental

The silicalite crystals (siliceous polymorph of ZSM-5) were grown in fluoride medium according to the protocol of Guth and Kessler[8]. Crystals are about 80x30x30 $\mu m^3$, with a regular elongated prismatic shape. For the neutron scattering experiments, a quantity of dmpNA corresponding to ~2 molecules per unit cell was sublimated under vacuum at 450 K and adsorbed for 48h in activated zeolite crystals in sealed glass tube. Afterward, the glass container was unsealed inside a glove box and the sample was transferred into an indium sealed aluminum container. NSE measurements were performed in a cryostat in the 150-300 K range under ambient pressure on a 4 mm thick sample, which contained a quantity of H atoms equivalent to 0.25 mm of $H_2O$ thickness.

The NSE experiments were performed on the MUSES spectrometer at the Laboratoire Leon Brillouin (LLB), Saclay, France. Time range from 1 ps to 100 ps was probed with an incident neutron wavelength of 5 Å. NSE is able to detect relative energy changes of 1 meV, despite a broad $\Delta$E/E energy bandwidth of the incident polarized neutron beam (15%). This is made possible by using the Larmor precession angle of the neutron spin in a controlled magnetic field as a measure of the energy transfer associated with the neutron-sample interaction[9]. An interest in using NSE to probe host dynamics in matrices such as zeolites is the simultaneous possibility of decoupling quantitatively the total scattered intensity into the coherent and incoherent part by polarisation analysis. The measured quantity in NSE is the polarisation of the scattered neutron beam (P) as a function of the wave-vector (Q) and the spin echo (Fourier) time (t). A scan of total scattered intensity (at fourier time t=0) was at first collected for Q = 0.2-1.9 Å$^{-1}$ with a step size of 0.1 Å$^{-1}$ to map the peaks of coherent scattering (Bragg reflections) from the zeolite matrix. Consequently, those wave-vectors with the maximum incoherent contribution stemming from the signal of H atoms of dmpNA were selected. The instrumental time-resolution of the spectrometer, $P_{res}$(Q,t), was measured with two standard elastic scatterers: graphite at Q = 0.35 Å$^{-1}$ and amorphous quartz at Q = 1.4 Å$^{-1}$. For the case of purely coherent or purely incoherent scattering, the normalised intermediate scattering function I(Q,t) is obtained from the measured polarisation, P(Q,t), according to the following equation:

$$I(Q,t) = \frac{P(Q,t)}{P(Q,0)} \times \frac{P_{res}(Q,0)}{P_{res}(Q,t)} \tag{1}$$

For cases of a mixture of coherent and incoherent scattering at a given wave-vector, Q, this simple treatment might not be sufficient, depending on the relative intensity of the two contributions. As for other systems containing a confining matrix, the pollution of the primarily incoherent scattering Q region by coherent scattering from adjacent Bragg peaks is likely to occur in the current system and thus care has to be taken in interpreting the I(Q,t) curves obtained using Equation (1).

I(Q,t) is the space Fourier transform of the van Hove space time correlation function[10]. As a general rule, the incoherent scattering function for local isotropic rotational motion can be written as the sum of two components (Equation (2))[10][11].

$$I(Q,t) = Ae^{-t/\tau} + (1-A) \tag{2}$$

The first term describes the quasielastic contribution, which decays with a characteristic relaxation time '$\tau$', while the second term is the elastic, time-independent component due to the local motion. The elastic part includes also contributions from immobile protons and residual background corrections.

## 3 Results

Total scattered neutron intensity and polarisation (at t=0) are shown in Figure 1a as a function of Q for the dmpNA-loaded MFI sample at 298 K. A very strong coherent scattering contribution, coming from Bragg reflections of the zeolite phase, is observed around 0.6 and two weaker contributions follow around 1.1 and 1.7 Å$^{-1}$. Due to the inherent low Q-resolution of the NSE spectrometer, the broadening of the Bragg peaks is significant, as seen in Figure 1a. In order to minimize the coherent contribution to the total scattering, we have chosen to measure the change in intensity and polarisation of the neutron beam in interaction with the sample, P(Q,t), in the Q-range below 0.6 Å$^{-1}$ and between 0.8 - 1.5 Å$^{-1}$. The choice was further narrowed by exploiting Q values for which the initial polarization (at t=0), was at least 5%.

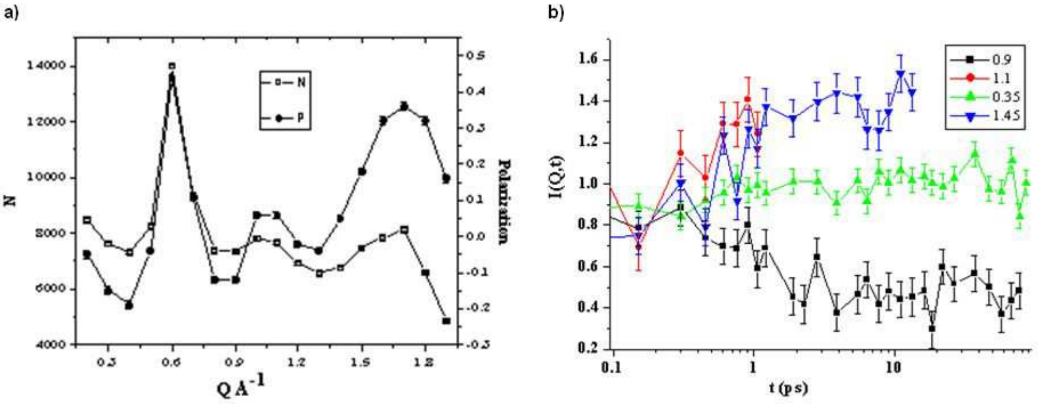

**Fig. 1.** a) The total scattered intensity (N, left axis) and polarisation of the neutron beam (P, right axis) versus momentum transfer (Q) collected on dmpNA encapsulated in silicalite. b) Intermediate scattering function calculated according to Equation (1) for dmpNA encapsulated in silicalite at 298 K: for Q = 0.35Å$^{-1}$, 0.9Å$^{-1}$, 1.1Å$^{-1}$ and 1.45Å$^{-1}$.

The intermediate scattering I(Q,t) functions were calculated from the measured polarisation, P(Q,t), according to Equation (1). They are plotted in Figure 1b for various Q at 298K, as a function of the neutron spin-echo time (t). Each I(Q,t) curve required about 22 hours of acquisition time. The behavior of the I(Q,t) curves at Q = 1.1 and at Q = 1.45 Å$^{-1}$ is influenced by the mixture of coherent and incoherent scattered intensity and is departing from the expected behavior of the function, i.e. a gradual decrease from 1 as a function of time. Considering that

$$P(Q,t) = A_{coh} - \frac{1}{3} A_{inc} I_{inc}(Q,t) \tag{3}$$

where $A_{coh}$ and $A_{inc}$ are the intensities of the coherent and incoherent scattering, the observed inverted behavior of I(Q,t) is a consequence of an incoherent (time-dependent) contribution being superimposed onto a more intense coherent static contribution. The assumption that the coherent scattering in this system is static is justified, as it originates from the confining matrix.

Regardless of the decrease or increase of the I(Q,t) curves in Figure 1b, the ensemble of the curves points strongly towards a non-dispersive, i.e. local, relaxation being probed, such as the methyl group rotation. This is supported by the fact that at low Q (0.35 $Å^{-1}$), no relaxation is seen, i.e. we are on a spatial scale larger than the local motion and at all other wave-vectors probed (0.9, 1.1 and 1.45 $Å^{-1}$), the relaxation occurs with a very similar characteristic time (1-2ps, as extracted from the data at 0.9 $Å^{-1}$).

To further support the presence of this non-dispersive fast motion, we have carried out supplementary time-of-flight measurements (TOF) on the MIBEMOL spectrometer in LLB, Saclay. Fitting the quasi-elastic signal observed at 300 K and Q = 0.8 - 1.0 $Å^{-1}$, the broadening obtained corresponds to a relaxation with a typical time of 1.3 ps, in agreement with the NSE data (Figure 2a, b).

The intermediate scattering functions measured at various temperatures at Q=0.9 $Å^{-1}$ are plotted in Figure 2a as a function of the spin-echo time 't'. The faster decay of the intermediate scattering functions with increasing temperature in Figure 2a reflects the increased motions of dmpNA protons. The relaxation times of the motions are obtained by fitting the I(Q,t) curves in Figure 2a using equation (2) plus a constant for residual background errors.

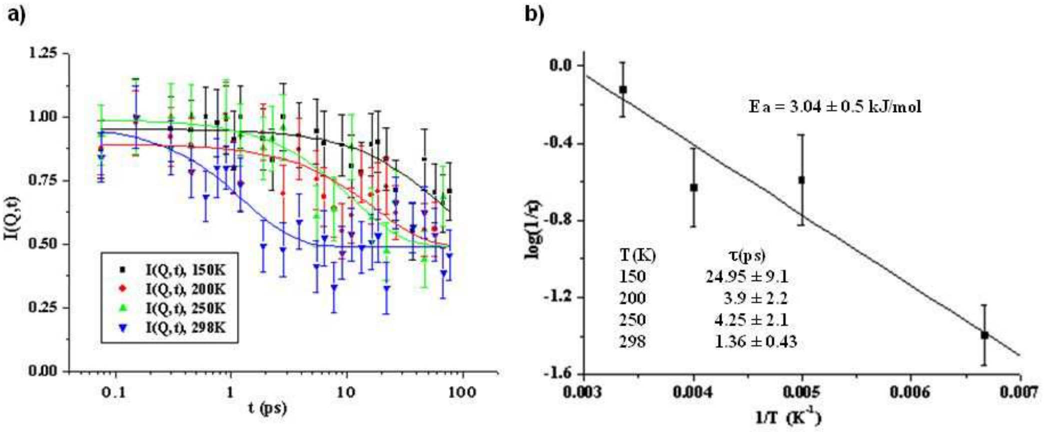

**Fig. 2.** a) Intermediate scattering function obtained for dmpNA encapsulated in silicalite at: 150 K, 200 K, 250 K and 298 K, for Q = 0.9$Å^{-1}$. b) Characteristic frequency '$1/\tau$' versus temperature 'T'. The solid line is the calculated Arrhenius law from a least squares fitting.

An Arrhenius plot of the relaxation times is displayed in Figure 2b. The characteristic frequency '$1/\tau$' is temperature dependent through the Arrhenius law and we have determined the activation energy, Ea=3.04±0.5 kJ/mol for the dmpNA-MFI composite.

## 4 Discussion

To our knowledge, this is a first report on the motion of dye molecules in zeolite (MFI) channels, using neutron scattering techniques. In previous studies, interference microscopy was used to investigate the intracrystalline diffusion of pyronine and oxonine dye molecules in zeolite L (suspension in water)[12]. The energy transfer from donor to acceptor dye molecules adsorbed in the channels of zeolite L had been used for measuring the diffusion kinetics. However, the values estimated for the diffusivities of dye molecules were very small and were influenced by counter diffusion of the solvent molecules. A neutron experiment was first performed by us on the back-scattering spectrometer IN16, ILL[13], with loading of 2 molecules per unit-cell, but the broadening of the elastic peak was too small to allow a diffusion coefficient to be extracted. Then, experiments were performed at the same dye-doping concentration with the spin echo spectrometer MUSES at LLB and emphasis was laid upon shorter times, 1ps - 100ps, in order to detect some local molecular motion. And indeed, from the present study, the activation energy determined for the motion of dmpNA in the MFI channels is what we may expect for end molecular group rotations. In order to compare our data with other results dealing with motions in solid systems containing end methyl groups, the rotational motion of the methyl group in pentafluoroanisole and in pentafluorotoluene is an excellent example recently reported where the dynamics of the methyl groups can be separated from the other molecular motions[14]. The incoherent neutron scattering from these molecules arises mainly from the methyl group protons and the observed dynamic effect can be assigned to their local motions. Activation energy of 2.7 kJ/mol is reported for methyl group rotations in pentafluorotoluene and this value is very close to the one we have obtained.

## 5 Conclusions

Using the neutron spin-echo technique, fast motions of dye molecules trapped in the zeolite channels have been studied successfully for the first time. The dmpNA dye molecules with dimensions nearly equal to the pore size of the MFI channel systems form stable organic-inorganic hybrids with the MFI zeolite. From our results and within the instrumental energy resolution and the temperature range used, it is inferred that dmpNA does not exhibit any long-range translational motion from one adsorption site to another throughout the MFI channels. Only the fast rotational motions of the end methyl group have been detected. This conclusion is consistent with recent QENS results in methyl group rotation studies[15]. The existence of end methyl and alkyl group rotations in an aromatic compound has been reported in the literature from QENS studies previously[14][16]. Activation energies deduced from these studies match well with ours for the methyl group rotations.

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